STEAM ELECTROLYSIS

The present invention relates to hydrogen production, and
more particularly to hydrogen production by high temperature
5   steam electrolysis with improved efficiency and reduced
cost.

Hydrogen is becoming an increasingly important fuel. Various
processes have been developed for producing it including
10   inter alia, steam reforming of natural gas and by coal
gasification, and water electrolysis. Existing processes
do, however, suffer from various disadvantages including
relatively low efficiency and high production costs.

15   It is an object of the present invention to avoid or
minimize one or more of the above-mentioned disadvantages.

It has now been found that by using a proton conducting
electrolyte membrane, which is substantially non-permeable
20   to oxide ions and to molecular gas, and is stable at high
temperatures, it is possible to dissociate water into
hydrogen and oxygen and at the same time separate the
hydrogen from the oxygen.

25   Thus in one aspect the present invention provides a method
of producing hydrogen comprising: providing a steam feed
stream, contacting said steam feed stream with a proton
conducting membrane supported on a porous redox stable
substrate, through said substrate, said membrane being
30   substantially non-permeable to molecular gas and to oxide
ions, applying a DC voltage across an anode coupled to the
substrate side of said membrane and a cathode coupled to the

other side of said membrane so as to dissociate at least part of said steam feed stream therebetween, into protonic hydrogen and oxygen at said anode, allowing said protonic hydrogen to pass through said membrane and form molecular

5 hydrogen at said cathode, and collecting said molecular hydrogen.

In another aspect the present invention provides a steam electrolyser for producing hydrogen, comprising: a dense

10 proton-conducting membrane substantially non-porous to molecular gas, said membrane being supported on a gas permeable, chemically and mechanically stable, electronically conducting substrate, said membrane being coupled: at the substrate - supported side to an anode for

15 connection to a positive voltage, and to a steam inlet and oxygen outlet for feeding a steam feed stream into said substrate and exhausting oxygen gas released therefrom; and at its other side to a cathode for connection to a negative voltage and a hydrogen gas outlet for exhaustion of hydrogen

20 gas released at said cathode.

It should be noted that in the simplest case the anode may simply form part of the substrate adjoining the membrane where a suitable substrate is employed i.e. where the

25 substrate material is electrochemically active. Alternatively the anode may comprise a thin layer of a different material interposed between the membrane and the substrate support.

30 With the present invention the hydrogen production process is substantially simplified, whilst having a relatively high efficiency, and uses apparatus of relatively economic

construction. The process provides hydrogen gas which is free from oxygen, steam and other gases, thereby avoiding the need for any downstream separation of gases. Also the electrolysis and separation out of hydrogen gas, may be

5   achieved without the need for any expensive precious metal catalysts or the like.

Various proton-conducting materials are known in the art which are stable to a greater or lesser extent at high

10   temperatures. In general steam electrolysis is carried out at temperatures of around 900 to 1000 °C. A particular advantage of the present invention is, however, that steam electrolysis can be carried out at significantly lower temperatures, for example, from 500 to 700 °C, whereby the

15   materials and construction used may be significantly simplified and reduced in cost. In general suitable proton-conducting materials comprise a material which allows the reversible dissociation of water into its lattice to form mobile protonic carriers therein. Such materials are

20   frequently oxygen deficient perovskites of formula ABO_{3-d} wherein A and B represent metallic elements occupying the A and B sites of the perovskite lattice structure and δ represents the degree of oxygen deficiency.

25   Particular preferred materials which may be mentioned include "$BaCe_{0.9}Y_{0.1}O_{2.95}$ (BCY10), $BaZr_{0.9}Y_{0.1}O_{2.95}$ (BZY) and members of the solid solution, $BaCe_{0.9-x}Zr_xY_{0.1}O_{2.95}$ (BCZY), or the analogues of the previously mentioned phases with lanthanides such as Gd, Nd or Yb instead of Y and such

30   phases with higher degrees of substitution such as $BaCe_{0.8}Y_{0.2}O_{2.95}$ (BCY20), $Sr_3CaZr_{0.5}Ta_{1.5}O_{8.75}$ (SCZTO) and

$Ba_3Ca_{1.18}Nb_{1.82}O_{8.73}$ (BCN18) as well as composites of such
materials. Thus, for example, there may be used a membrane
comprising a layer of BCY10 which has relatively high
electrochemical performance (in terms of proton conduction)
in contact with the substrate on the hydrogen side, with an
outer protective layer of SCZTO which has better stability -
especially against chemical degradation by atmosphere CO_2.
Similarly on an oxidising-side supported electrolyte the
$BaCe_{0.9}Y_{0.1}O_{2.95}$ (BYC10) may be protected from the high steam
atmosphere by a layer of a material such as SCZTO or BZY.

As indicated above, it is also important that the membrane
should be substantially impermeable to molecular gas.
Accordingly the membrane material needs to be in a
substantially dense, non-porous, form. The membrane is also
substantially impermeable to oxide ions.

In order to maximize the efficiency of the electrolyser, the
resistivity of the membrane should be kept as low as
possible. Desirably therefore the membrane should be as
thin as is reasonably practicable. Preferably the membrane
thickness is not more than 25 μm, advantageously from 1 to
25 μm, most preferably from 3 to 15 μm.

It is also important that the membrane should remain stably
attached to the substrate support under the high temperature
operating conditions of the electrolyser. Various methods
are known in the art for forming thin films on substrates
including inter alia: sol-gel techniques in which a liquid
suspension is applied to a substrate, dried and then cured;
tape casting in which the membrane material is provided in a
powder form embedded inside a polymer tape which is placed

on the surface of the substrate and heat treated to form a
substantially continuous film of membrane material; vacuum
deposition in which the membrane material is provided in a
powder form suspended in a liquid carrier is placed on the
5   surface of the substrate and drawn into the surface thereof
by means of a vacuum applied to the remote side of the
porous substrate, and then heat treated to form a
substantially continuous film of membrane material at the
substrate surface; etc. It will be appreciated in relation
10   to such processes that, in accordance with normal practice,
the particle size of the membrane material applied to the
surface of the porous substrate should not be significantly
less than the pore size of the substrate, in order to
minimize penetration of the particles into the interior of
15   the substrate. Using such techniques we have successfully
obtained proton conducting ($Sr_3CaZr_{0.5}Ta_{1.5}O_{8.75}$) membrane films
on porous conductive substrates (Ni:YSZ and LSM,
$La_{0.8}Sr_{0.2}MnO_3$) with film thicknesses in the range from 3 to
100 microns, depending on the number of layers deposited.
20

Membranes of $BaZrO_3$-based materials are especially preferred
as these are stable and exhibit high proton conductivity.
Those materials have, though, to be sintered at a
temperature above 1600°C which makes it very difficult to
25   find suitable electrode materials which have so high a
melting point without undergoing significant chemical
reactions with the $BaZrO_3$-based electrolyte. By using a
sintering aid such as ZnO, it is, however, possible to
reduce substantially the sintering temperature, whilst still
30   obtaining a high density product and substantially
maintaining the desirable properties of high proton
conductivity and stability. More particularly we have found

that by using a relatively small amount of ZnO - typically
around 1% w/w, it is possible to reduce the sintering
temperature of $BaZr_{1-x}Y_xO_{3-x/2}$ from around 1700°C to around
1300°C, albeit desirably a sintering temperature of at least
5   1350°C should normally be used, and obtain a high density
material with a relative density of the order of 96%.

In general suitable sintering aids comprise Al_2O_3, Bi_2O_3 and
some first row transition elements oxides such as TiO_2, Fe_2O_3,
10 CoO, CuO etc, which are commonly used as sintering aids for
obtaining dense ionic conducting materials such as yttria
stabilised zirconia (YSZ) and ceria doped with gadolinia
(CGO).

15 In order to have a significant effect in reducing the
sintering temperature, it is generally necessary to use a
minimum amount of the sintering aid. This can be readily
determined by trial and error and is typically of the order
of from 0.1 to 0.5 %w/w. In order to avoid significant
20 distortion of the membrane material structure and adverse
effects on the proton-conducting and stability properties
thereof, it is generally desirable that the amount of
sintering aid should be minimized - whilst still maintaining
a useful sintering temperature reduction. Desirably there
25 should be used not more than 5 %w/w, preferably not more
than 2 %w/w, of sintering aid.

The sintering mechanism is typically due to the formation of
low melting phases between the sintering aid and constituent
30 oxides, which lower the sintering temperature. Alternatively
the sintering aid enters the oxide lattice and produces a
lower melting phase that sinters more readily. In either

mechanism the sintering aid may be lost on sintering. Without in any way wishing to restrict the scope of the present invention, it is believed that in this case it seems that the sintering aid acts as a dopant that essentially replaces some of the B-site ions and the solid solution $BaZr_{1-x-z}Y_xM_zO_{3-z-x/2}$ forms wherein M represents a dopant metal and Z represents the level of B-site ion replacement and is typically in the range from 0.05 to 0.25, preferably at least 0.1. Suitable dopants include one or more oxides of M = Al, Ti, Bi, B, Mn, Mg, Zn, Co, Ni, Fe, Cu, especially Zn. The mentioned elements may be added into the materials in the form of oxide, carbonate, nitrate, chloride, carbide, nitride, etc and, through any method such as solid state reaction, sol-gel process or any form and technology known as the art. It will be appreciated that some sintering aids are more effective than others and that some sintering aids will require higher concentrations thereof. In this connection Zn doped oxides are particularly good low temperature sintering aids. Preferably substantially pure ZnO is used. In general the amount of dopant used may be from 0.1 to 5 % w/w, preferably 0.5 to 3% w/w. In the case of ZnO there is conveniently used about 1% w/w of the ZnO.

The use of such sintering aids is similarly beneficial with other membrane material such as Barium Yttrium Cerate and especially Barium Yttrium Cerate Zirconate which combines stability and conductivity performance.

Various porous electrically conducting materials which are stable at the elevated temperatures used in steam electrolysers are already known in the art, and may be used for the substrate support in the present invention.

Suitable materials generally comprise a metallised ceramic or a mixed conductive oxide having an electrical conductivity of not less than 10 Scm^{-1}, preferably not less than 100 Scm^{-1}, at the operating temperature of the steam

5   electrolysis. Particular suitable substrate materials which may be mentioned include metallised ceramics such as $Cu:Al_2O_3$ or mixed conductive oxides such as $La_{0.8}Sr_{0.2}MnO_3$ (LSM), chromium-doped LSM (i.e. $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$) or $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ (LSCF).

10

As indicated above, the substrate support requires generally to be sufficiently porous to facilitate penetration of the steam molecules to the membrane and to facilitate exhaustion of oxygen molecules exiting from the membrane. In general

15 therefore the pore size should be not less than 0.5 µm, and conveniently from 0.5 to 10 µm. Desirably the porosity is from 30 to 60 %, preferably from 40 to 50%. Where such a discrete anode is provided between the membrane and the substrate, it will be appreciated that in such cases the

20 membrane is supported indirectly by the substrate. Generally in such cases the anode layer is deposited on the substrate, and then the membrane layer deposited onto the anode layer. Various techniques are known in the art, including those descried elsewhere herein, for producing

25 thin film layers onto substrates of various kinds.

As noted above, a thin layer (generally 10 to 100 µm, preferably 30 to 50 µm) of the substrate support itself may conveniently function as the anode of the electrolytic

30 apparatus, (where the substrate material is electrochemically active), and is connected to the voltage

supply via a porous metal current collector in generally
known manner. A porous cathode requires generally to be
sufficiently porous to facilitate exit of hydrogen molecules
from the membrane. In general therefore the pore size

5   should be not less than 0.5 μm, and conveniently from 0.5 to
10 μm. Desirably the porosity is from 30 to 60 %,
preferably from 40 to 50%. The cathode may be provided on
the surface of the membrane electrolyte by painting, screen
printing or sol-gel coating, and is connected to the voltage

10   supply via a porous metal current collector in generally
known manner. Suitable cathodes are conveniently of a
transition metal such as porous metallic platinum or
palladium, or a Ni cermet of a transition metal and a proton
conducting electrolyte. Various mixed conducting oxides

15   which may also be used, are known in the art including
perovskite oxide materials such as those disclosed in
WO2004/013925.

One of the benefits of the invention is that the lower

20   working temperatures allow the use of less expensive current
collector metals such as steel, which may, if desired, be
provided with electrically conducting protective film
coatings, e.g. of chromium.
(as well as avoiding the use of expensive precious metal

25   catalysts etc).

The substrate supported membrane, electrode, and current
collector, assembly may be electrically insulated from the
gas supply and exhaust pipes and any external housing, which

30   are generally made of metal e.g. steel, by means of a high

temperature glass ceramic such as barium silicate or a high
temperature cement.

As indicated above the steam electrolysis may be carried out
5   at a range of different temperatures. It will also be
understood that higher temperatures have the advantage of
reducing the direct electrical energy input required. It
is, however, a key feature of the present invention that it
allows the use of lower temperatures than have been used
10 heretofore in steam electrolysis, which in turn allows the
use of significantly more economic materials and forms of
construction. It is also important to avoid using higher
temperatures as these can result in oxide ion conductivity
developing in the membrane and even permeability to water
15 molecules. Preferably there is used an operating
temperature of from 400 to 800 °C, most preferably from 500
to 700 °C.

In general it is convenient to use a steam supply at a
20 temperature substantially equal to the desired operating
temperature at the membrane. It is also possible though to
supply steam at a lower temperature and to heat the
substrate supported membrane, e.g. using an external
electrical or fuel gas (conveniently hydrogen), furnace.
25

It will also be understood that the voltage required to be
applied across the membrane for a given hydrogen flux will
depend on the electrical resistance of the membrane, and any
supporting substrate employed. The electrical resistance
30 will in turn depend on the particular materials used, as
well as the thickness thereof, and the operating temperature
used. It is accordingly desirable that the membrane should

be as thin as is reasonably practicable i.e. whilst still
maintaining gas tightness and structural integrity under the
operating conditions used.   Typically we have found that
useful levels/rates of electrolysis may be obtained with an
5   applied voltage of the order of 1.1 to 1.2 V when using a
proton conducting ($BaCe_{0.9}Y_{0.1}O_{2.95}$, $Ba_3Ca_{1.18}Nb_{1.82}O_{8.73}$, etc)
membrane having a thickness of around 25 μm.

The feed stream may be supplied to the electrolysis
10 apparatus at ambient pressure.   Steam generators, though,
generally provide steam at super-atmospheric pressures and
the use of such higher pressures – typically up to 10 bar or
even 100 bar - has the advantage of increasing efficiency.

15 The steam feed stream is generally supplied to the module
via piping connected to the module so that the feed stream
is passed across the surface of the substrate and
undissociated steam together with oxygen produced are then
carried away.   At the cathode side, hydrogen gas produced is
20 also generally exhausted by suitable piping.   The piping
(and conveniently also any external support such as a
manifold or housing, for the substrate-supported membrane)
may be made of any material known in the art but may
conveniently be of steel or alumina, or the like.
25

The steam feed stream is generally contacted with the
substrate support, by passing a flow thereof across the
exposed surface thereof.

30 Further preferred features and advantages of the present
invention will appear from the following detailed

description given by way of example of some preferred

embodiments described with reference to the accompanying

drawings in which:

Fig.1 is a schematic section through a steam electrolyser

5 module of the invention; and

Fig.2 is a schematic perspective view of a manifold

interconnector for a multi-module electrolyser.

Fig.1 shows a steam electrolyser module 1 of the invention

10 mounted in a manifold 2 and coupled to gas flow pipes 3,4 at

cathode and anode sides 5,6 thereof, respectively. In more

detail, the module 1 comprises a 5 µm thick dense non-porous

proton-conducting membrane 7 of BCY10 or BCN18 deposited on

a 2 mm thick LSM substrate 8 having a 40% porosity and a

15 pore size generally in the range of from 0.5 to 10 µm.

On the outer face 9 of the membrane 7 (remote from the

substrate support 8) is provided a porous metallic platinum

cathode or hydrogen electrode 10, on top of which is

20 provided a steel mesh current collector 11 connected 12 to

the negative pole 13 of a DC voltage supply 14. At the

anode side outer face 6 of the substrate 8 is provided a

steel mesh current collector 15 connected 16 to the positive

pole 17 of the DC voltage supply 14 so that a positive

25 voltage is applied to a thin (30 µm thick) layer 18 of the

substrate 8 adjacent the membrane 7, which functions as an

anode or steam electrode. The module 1 is electrically

insulated from the steel manifold 2 and pipes 3,4 by a high

temperature barium silicate glass ceramic seal 19.

30

The anode side pipe 4 has an inlet branch 4a through which high temperature steam 20 is fed in and passed across the exposed anode side outer face 6 of the substrate 8. Any undissociated steam 21, together with oxygen 22 produced by

5 the electrolytic dissociation of the steam feed, are exhausted by an outlet branch 4b of the anode side pipe 4. The cathode side pipe 3 is used to exhaust hydrogen gas 23 liberated at the cathode 10.

10 In use of the above module the following processes occur:

at the anode $2H_2O \rightarrow 4H^+ + O_2 + 4e^-$

at the cathode $4H^+ + 2e^- \rightarrow 2H_2$

Fig. 2 shows part of a large scale steam electrolyser

15 comprising a manifold interconnector 24 mounting multiple modules 1 such as those of Fig. 1.

Example 1 - Preparation of Proton Conducting Membrane Material

20 A nominal $BaZr_{0.8}Y_{0.2}O_{2.9}$ powder was prepared by a solid state reaction method. For example, 9.8675g $BaCO_3$, 4.9288g ZrO_2 and 1.1291g Y_2O_3 powders were dried at 500-700°C before mixing together and ball-milling in a zirconia container with zirconia balls. The mixture was fired at 1400°C for 10

25 hours.

The required amount of sintering aid was mixed together with as-fired powder, ball-milled for 15 minutes twice, then pressed into pellets having a diameter of 13mm, before

30 firing at 1350°C. Pure ZnO was used as the sintering aid and a dense $BaZr_{0.8}Y_{0.2}O_{2.9}$ pellet was obtained. To minimise the effect of addition of ZnO on the other properties such as

its conductivity, the amount of ZnO added was kept to a

minimum. Less than 1wt% of ZnO, however, would require a

higher temperaturein order to effectively sinter the

$BaZr_{0.8}Y_{0.2}O_{2.9}$ pellets.

5

With the addition of only 1 w/w % ZnO, $BaZr_{0.8}Y_{0.2}O_{2.9}$ pellets

may be readily sintered at a temperature as low as 1350°C. A

relative density of 96% was obtained after firing the

$BaZr_{0.8}Y_{0.2}O_{2.9}$ pellets at 1350°C for 10 hours with addition of

10 1wt% ZnO. For comparison, pellets pressed from 1400°C/10h

$BaZr_{0.8}Y_{0.2}O_{2.9}$ powder without any ZnO, were also fired at

1350°C for 10 hours together with the pellets with 1wt% ZnO

sintering aid. The latter were found to have a much lower

relative density of only around 68% and cracked into powders

15 after exposure to air for just a few days.

Example 2 - Preparation of Membrane Material using direct

solid state reaction to incorporate zinc into the lattice.

20 $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{2.88}$ was prepared using 9.8675g $BaCO_3$,

4.3030g CeO_2, 1.8483g ZrO_2, 0.9032g Y_2O_3 and 0.1627g ZnO,

which were mixed together and ball-milled at high speed in

zirconia container with zirconia balls for 15 minutes twice

with addition of acetone. The mixture was dried to remove

25 the acetone, then pre-fired at 1100°C for 2 hours. The as-

fired powders were pressed into pellets 13mm in diameter or

fired at 1300°C for 10 hours. Dense pellets with relative

density over 96% were obtained by this process. This Example

shows that $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ was fully sintered at 1300°C

30 by introducing a small amount of zinc at the B-site and that

ZnO is an effective sintering aid for low temperature
sintering of $BaCeO_3$ and $BaCe(Zr)O_3$-based perovskites.

Example 3 - Properties of Membrane Material

5 The conductivity of the material obtained in Example 2 was
measured by ac impedance spectroscopy and the total
conductivity found to compare favourably with previous data
as shown in Figure 3. A pellet of the material (thickness
1.453 mm) was investigated in a concentration cell with

10 platinum electrodes between hydrogen and oxygen passing
through room temperature water. The open circuit potential
using the above described membrane material decreased with
increasing temperature as oxide transport started to compete
with proton conduction as shown in Figure 4. This is

15 expected behaviour for an intermediate temperature proton
conductor.

Example 4 - Fabrication of a dense proton conducting thin
film membrane on a porous substrate.

20 Porous $La_{0.8}Sr_{0.2}MnO_3$ (LSM) substrates were prepared by tape
casting. The liquid mixture used for tape casting consists of
commercial submicron-size LSM powder (Praxair), graphite
powder used as pore former, a (3:1) mixture of methyl ethyl
ketone and ethanol as solvent, polyethylene glycol and di-n-

25 butyl phtalate as dispersant and plasticizer, respectively
and polyvinyl butyral resin binder (commercially available
as Butvar®B-98). The mixture comprising powder, solvent (1:1
mixture to the powder) and pore former (40 wt%) was ball
milled overnight on a roller ball mill using zirconia balls

30 for breaking the agglomerates and reducing the particle
size. The organic additives (dispersant, plasticizer and
binder, also 40wt% referring to LSM) were then added and the

slurry was mixed in an electrical shaker for half an hour.
The organic additives are meant to increase the viscosity of
the slurry and to add strength and flexibility to the green
tape. A subsequent ball milling for 4 hours is performed for
5   homogenization of the slurry. The slurry was then used for
green tape deposition using a tape casting machine and the
resultant dried tapes were cut, overlapped and cut into 2.5
cm diameter disks. The disks were then fired with a slow
ramp rate of 0.5°C to 1000°C for burning the organic
10 residues, kept there for 5 hours and then fired to 1300°C
for sintering and increasing the mechanical strength. The 2
cm diameter porous LSM disks presents around 50% porosity
and a rather uniform distribution of micron size pores
within the structure. In most of the cases, a thin layer of
15 $La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O_{3-x}$ (LSCM) as a buffering layer was deposited
by spray coating to prevent the reaction between the LSM
substrate and $BaCe_{0.5}Zr_{0.3}Y_{0.16}Zn_{0.04}O_{3-\delta}$ (BCZZY) electrolyte. The
slurry used for spraying was prepared in a similar manner as
above, increasing the amount of solvent used. The as
20 prepared substrates are placed on a hot plate and held at
about 300-350°C while about 10 ml of electrolyte suspension
(2 g BCZZY ultrasonically dispersed in a mixture containing
35 ml ethanol) was sprayed onto the substrate using an
airbrush. During deposition it must be ensured that the
25 suspension hits the surface of the substrate while wet,
allowing the remaining solvent to wick into the porous
substrate before evaporation and avoiding solution pooling.
The green bilayer is then sintered to 1325-1350°C for 5
hours using an alumina disk placed on top of the eletrolyte
30 to ensure flatness of the assembly. The resulted structure
was a porous LSM substrate deposited with a less porous,

very thin layer of LSCM and a dense film of BCZZY of
approximately 10-40 microns thickness. An electron scanning
micrograph of a cross section through a sample of the
structure is shown in figure 5.

5

Example 5 - Laboratory test of a steam electrolyser assembly
with a BCZZY membrane

An LSM-BCZZY substrate-membrane assembly generally similar

10   to that illustrated in Figure 1 was prepared by tape-casting
(substrate) and spray-coating (membrane) as described in
Example 4 above. The BCZZY-membrane was about 40 μm thick
and was provided with a porous Palladium Cathode. At the
Anode there was provided a Platinum mesh Anode/current

15   collector. The steam feed stream (to the Anode) used a pure
oxygen supply as a carrier for the steam in order to avoid
possible contamination of the cell components.

The steam partial pressure of the steam feed stream gas was

20   controlled by bubbling the gas through a water bath that was
kept at ambient temperature in this instance achieving a
steam partial pressure of 0.022 bar and providing a gas
composition of 2.2 vol% H_2O and 97.8 vol% O_2, to the Anode. A
gas mixture comprising hydrogen and argon was similarly

25   bubbled through ambient water to supply a gas having a
composition of 2.2 vol% H_2O, 5 vol% H_2 and 92.8 vol% Ar to
the cathode. Each of the gas flows was typically adjusted
to 200 ml/cm^3.

30   The amount of hydrogen produced was determined from the
potential on a zirconia oxygen sensor using the Nernst

equation and the water dissociation equilibrium constant as
detailed below in equations (1) and (2). The zirconia oxygen
sensor was positioned in the exit gas flow and was kept at T
= 766 °C. At zero applied current and an electrolysis cell
5 temperature of 605 °C, the gas partial pressures in the gas
mixture were $pO_2 = 1.125 \times 10^{-20}$ bar, $pH_2O = 0.0223$ bar and pH_2
= 0.0496 bar (at 766 °C).   When a constant current of 15 mA
was applied to the electrolysis cell, the change in
potential, E, of the cell is shown in Fig. 6. From the
10 voltage output, EMF, of the zirconia sensor, and using
equations (1) and (2) below, it was calculated that pO_2
decreased to 9.840×10^{-21} bar, which corresponded to an
increase of pH_2 to 0.0531 bar and a conversion of ca. 16% of
the steam that was contained in the gas mixture supplied to
15 the anode, to hydrogen gas released at the cathode.

$$EMF = (RT/4F)\log_e(P_1(O_2)/P_2(O_2)) \qquad (1)$$

$$K_f = p(H_2O)/(p(H_2) \cdot (p(O_2))^{\text{½}}) \qquad (2)$$

20

wherein E, R, T, and F represent cell voltage, the Gas
constant, temperature and the Faraday constant, respectively
and K_f is the thermodynamic equilibrium constant for the
dissociation of water to hydrogen and oxygen, $H_2O \quad H_2 + O_2$.

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